



U.S. Department of Energy
Energy Efficiency and Renewable Energy

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Sulfur Removal and Gasification Membranes

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- **Project Background**
- **Technical Feasibility and Risks**
- **Competitive Advantage**
- **Project Overview**
- **Plan**
- **Summary**



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- Refocus of the thermochemical conversion program resulted in two evaluation efforts:
 - Sulfur removal in syngas systems
 - The use of membranes in gasification systems
- Evaluations began May 2005



Pathways and Milestones – C-level and Project Milestones

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Perennial Grasses

Woody Crops

Pulp and Paper

Forest Products

Aq Residues

Validate Cost-effective Gas Cleanup Performance

M 4.11.3

M 5.11.3

M.6.3.4

M 7.1.4

M 4.12.3

M 5.12.3

Validate integrated gasification and gas cleanup at pilot scale

M 4.11.5

M 5.11.5

M.6.3.5

M 7.1.5

M 4.12.5

M 5.12.5

Project Milestones	Type	Performance Expectations	Due Date
Costs of sulfur removal from biomass syngas	E	Detailed report on the cost of sulfur removal from syngas	31 Aug 2005
Evaluation of gasifier membranes	E	Summary report evaluating the overall concept of gasifier membranes	30 Sept 2005



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Sulfur Removal Evaluation

All downstream synthesis processes require removal of sulfur

- Objective of evaluation:
 - To document sulfur compositions and its forms in biorefinery feedstocks
 - To determine the pathways for sulfur species during gasification
 - To determine preferred sulfur removal processes for various H₂S/COS levels,
 - To develop process flow sheets,
 - To develop up to date economics
- Refocused effort in FY2005
- Evaluation being performed by Nexant, reviews and input by NREL & PNNL
- The evaluation supports all milestones for production of fuels & chemicals from syngas



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- Sulfur removal or control is required for technical feasibility of all thermochemical fuels and chemicals processes
 - Syngas hydrogen sulfide contents range from 100 ppm (clean wood) to > 2.5% (Kraft black liquor)
 - H₂S/COS removal will involve existing commercial processes



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Main Technology Types

1. Chemical Solvents

- Loose chemical bond formed with H_2S in absorber, H_2S released in stripper column
- Usually an amine solution; amine selected depends on process and selectivity requirements
- Preferred by natural gas industry

2. Physical Solvents

- “Dissolves” H_2S and CO_2 in solvent; common solvents are chilled methanol and ethers
- Low temperatures, high pressures preferred
- Process set-up similar to chemical solvent system

3. Combination Chemical/Physical Systems



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Other Technologies

1. Sulfur Recovery

- Claus Sulfur Recovery (high H_2S concentration, >20 TPD S)
- Oxidation/Reduction Sulfur Recovery (LO-CAT[®] and SulFerox[®])

2. Catalytic Absorbents

- Zinc or Iron Oxides
- Used as a polishing step or as a guard bed in applications that require very low S



Sulfur Process Summaries

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	Emissions	Manufacturers	Commercial Use	Applications and History
Chemical Solvents	Acid gas, waste water, small vent stream Indirect emissions from power requirements	Dow, UOP, Union Carbide, BASF, Shell, Others	NG processing, refining, IGCC	1000+, use in NG and refining for decades
Physical Solvents	As above, usually more power required	Lurgi, UOP, Uhde, Coastal	Reforming, gasification, ammonia and methanol synthesis	~150, first development in 1950s-1960s
Sulfur Recovery	SO ₂ from tail gas, pure sulfur (60 to 99%)	Most major engineering firms (Parsons, Ortloff, etc.)	NG processing, refining, gasification	1000+ Claus (early 20 th century), ~300 redox units (1970's)
Catalytic Absorbents	Spent catalyst	Synetix, Unicat	Reforming, very low S applications (liquids synthesis)	Many chemical applications, since 1980's



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Evaluation of Gasifier Membranes

- **Goal:** Examine the technical and economic feasibility of using membrane systems located inside or immediately downstream from a biomass gasifier
- **Approach:**
 - Determine if appropriately robust materials are available
 - Determine effectiveness of membranes in the presence of particulates, alkali, tars, and other typical biomass impurities
 - Determine if there is basic technical/economic potential
- Began in May 2005
- Evaluation is being performed by PNNL & NREL
- Supports milestones for syngas production efficiency and syngas quality in multiple pathways



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Included: Membrane systems for possible use in biomass syngas systems

- Membrane systems inside the hot zone of the gasifier or in close proximity downstream
 - Metal membranes
 - Ceramic membranes
- Representative functions:
 - Oxygen enrichment
 - Tar cracking
 - Product gas shift
 - Product recovery
 - Others

Not included:

- Stand-alone systems such as separate air enrichment
- Cool or cold gas filtration systems
- Others not specifically related to the biomass gasification system



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Issues to be addressed:

- **Thermal issues**
 - Stability at temperature
 - Thermal cycling stability
- **Particulate issues**
 - Plugging
 - Erosion and corrosion
 - Tar reactivity
- **Economic issues**
 - Impacts of membranes on the integrated biorefinery
 - Outcome will be an overall assessment of the feasibility of these types of membrane systems



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- Projects are a one-time evaluation of opportunities/needs
- Results are expected to guide overall economic analysis and program planning



Project Budgets

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Project	FY 04	FY 05	FY 06 Plan
3.2.4.4 Evaluation of Gasifier Membranes	0	300	0
3.3.1.4 Sulfur Removal From Syngas	0	300	0